must be weighed when considering rubber production from sunflower.

No attempt has been made to maximize the potential of rubber content through breeding nor to evaluate the remaining 31 species of *Helianthus*. The rubber content of the two closely related commercial varieties, Hybrid-896 and Hybrid-894, indicated that a wide variation occurs when no attempt is made to maximize rubber yields; thus, the potential for improvement exists. Our analysis also showed that the ornamental Mexican sunflower (*Tithonia rotundifolia*) has over 2% of a lower molecular weight rubber. Moreover, sunflower is already a profitable crop. Breeding techniques, planting methods, environmental influences, and major pests are already known.

Rubber production from sunflower could be an economic bonus. The residue from the plant extraction might also be a useful commodity, since residues of sunflower plants are ranked near the top for btu value (Oursbourn et al., 1978). Thus, a facility for processing rubber from sunflower might also be an ideal site for energy production from biomass. Additional research is needed to completely assess the potential of rubber production from sunflower.

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Direct Analysis of the Wild Oat Herbicide, Asulam, in Wheat Samples by Reversed-Phase Liquid Chromatography at Selected Ultraviolet Wavelengths

The wild oat herbicide asulam (methyl *N*-(4-aminobenzenesulfonyl)carbamate) was extracted from whole and refined wheat flour and whole wheat cereal with acetonitrile. An aliquot of the extract was partitioned with hexane which removed much of the lipophilic coextractives. The acetonitrile layer was then evaporated to about 0.2 mL and diluted with mobile phase to 1.0 mL for liquid chromatographic analysis. Separation of asulam from other sample components was achieved with a Lichrosorb RP-8 column and a mobile phase consisting of 20% (v/v) acetonitrile in water containing 0.1% acetic acid. Detection limits were estimated to be 0.02–0.05 ppm with an average recovery of about 87% over the range 0.1–10.0 ppm in the products studied.

INTRODUCTION

Asulam (methyl *N*-(4-aminobenzenesulfonyl)carbamate) is a systemic herbicide used in the prairie regions of Canada for the control of wild oats in cereal grains such as wheat. It is one of the five wild oat herbicides which accounted for about 50% by weight of all pesticides used in Canada in 1976. At the moment, the only methods available for asulam determination are a colorimetric procedure which employs diazotization with *N*-(1-naphthyl)ethylenediamine (Brockelsby and Muggleton, 1973) and a gas chromatographic (GC) technique (Bardalaye et al., 1979) which involves hydrolysis and derivatization. We describe in this paper a liquid chromatographic (LC) method which is capable of determining asulam in wheat products without derivatization. As a result the technique is simpler and more rapid than either of the above-mentioned techniques and may be easily incorporated into routine pesticide screening programs. The approach is intended to serve as a part of a direct LC multiresidue screening technique for all five wild oat herbicides in cereal grain products.

EXPERIMENTAL PROCEDURES

Reagents. Distilled-in-glass grade solvents were used for sample extraction and preparation of the standards. Stock solutions of asulam were prepared in acetonitrile at a concentration of 1.0 mg/mL. Spiking solutions were prepared from this by diluting with acetonitrile as required. Standards for LC were prepared by dilution of the stock with the mobile phase.

The wheat products examined were whole wheat cereal and whole and refined wheat flour.

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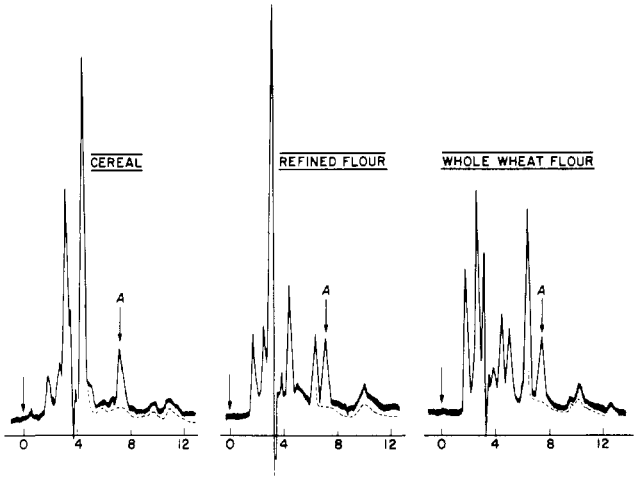

Figure 1. Chromatograms of asulam (A) spiked at 0.1 ppm in cereal and flour. Detection wavelength, 268 nm; attenuation, 0.01 absorbance unit (AU) full scale. Other conditions as described in the text. Dashed line represents sample blank background.

Liquid Chromatography. The LC system consisted of a Waters Model 6000A pump for solvent delivery and a Waters Model 450 variable wavelength detector (8-μL cell volume) set at 268 nm and 0.01 absorbance unit full scale. Wavelengths of 254 and 280 nm were also studied for comparison employing a Waters Model 440 fixed-wavelength UV detector. Separations were achieved on a 25 cm × 3.2 mm (i.d.) Lichrosorb RP-8 column with a mobile phase consisting of 20% (v/v) acetonitrile in water containing 0.1% acetic acid, at a flow rate of 1.0 mL/min at 20 °C. The sample injection volume was 25 μL throughout. Retention time of asulam was 7 min.

Sample Extraction. A 25-g sample of wheat product was homogenized with 70 mL of acetonitrile in a Sorvall Omni Mixer at medium speed (setting 5) for 2 min. The mixture was suction filtered through a 150-mL medium porosity sintered glass funnel into a 250-mL flask. The residue was rinsed with 30 mL of acetonitrile and the filtrate trasferred to a 100-mL volumetric flask and made up to volume with acetonitrile. A 20-mL aliquot representing 5 g of sample was transferred to a 100-mL separatory funnel containing 20 mL of hexane previously saturated with acetonitrile. After the mixture was shaken by hand for 1 min, the procedure was repeated with a second volume of hexane. The acetonitrile layer was collected in a 100-mL round-bottom flask and evaporated at 40 °C to ~0.2 mL. Care must be taken not to allow the residue to evaporate to dryness or losses will result. The residue was then quantitatively transferred with several washings of mobile phase to a graduated 5-mL centrifuge tube and adjusted to 2.0 mL or other appropriate volume with mobile phase for LC analysis.

RESULTS AND DISCUSSION

The chromatographic system described above functioned well for asulam throughout the analyses. The acetic acid was necessary to suppress ionization of the acidic herbicide (pK_a = 4.82); otherwise strong tailing and inconsistent retention times resulted. The response (peak height) of the detector to asulam was 0.6 cm/ng at 268 nm (initially selected since it was at the absorption maximum of asulam).

Figure 1 shows chromatographic results of the analysis of three wheat samples spiked at 0.1 ppm with asulam. The herbicide was easily detected at the spiking level in all three commodoties. Both flour samples contained a peak that eluted just in front of the asulam but which did not interfere with the quantitation.

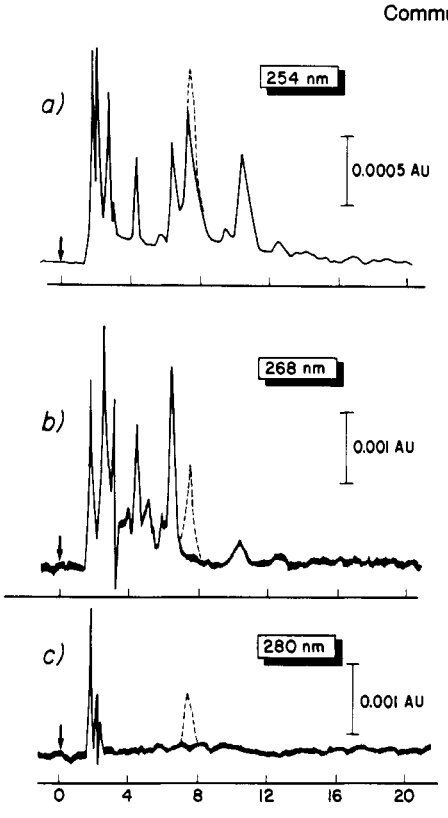

Figure 2. Chromatograms of a whole wheat flour extract: (a) 254 nm, 0.005 AU full scale; (b) 268 nm, 0.01 AU full scale; (c) 280 nm, 0.01 AU full scale; 62.5 mg of equivalent sample injected in each case. The dashed lines represent the response to 6.25-ng asulam in spiked samples (0.1 ppm).

Since asulam had appreciable absorbance at both 254 and 280 nm, several samples were analyzed at these wavelengths for comparison. This was carried out to assess the potential of fixed-wavelength UV detectors (in this work, a Waters Model 440) which all employ 254 nm and usually have accessory filters for operation at 280 nm. These detectors are advantageous in terms of their cost and sensitivity (signal/noise ratio) compared to variable wavelength detectors which make use of monochromators for wavelength selection from a continuum source (deuterium or tungsten lamps). In terms of absolute response to asulam (peak height, cm/ng at 0.01 absorbance unit full scale) 268 nm was most sensitive (0.6 cm/ng) compared to 254 nm (0.3 cm/ng) and 280 nm (0.3 cm/ng). However, on the basis of a signal/noise ratio (3:1), 254 nm on the fixed-wavelength filter detector proved to be most sensitive (0.6 ng was equivalent to 3× noise) while for the same signal:noise ratio, 280 nm required 2.0 ng and 268 nm, 3.0 ng (Waters Model 450). Since the signal:noise ratio was best for 254 nm, it was possible to increase the detector sensitivity setting to 0.005 absorbance unit full scale, inject much less sample, and still obtain sufficient peak height for quantitation. The injection of small samples is desirable in trace analysis in order to keep column contamination to a minimum, thus prolonging its lifetime. This is especially important for routine analysis.

However, sensitivity is not the only criteria for determining optimum detector wavelength. While 254 nm proved to be the most sensitive in terms of signal:noise, it was the least selective for the samples studied in this work. Figure 2 compares results of a whole wheat flour extract analyzed under the three detector wavelengths. As can be seen, 280 nm provided the cleanest chromatograms because of the absence of peaks from coextractives. The 254-nm setting was not useful because of an interfering

Table I. Recoveries of Asulam in Spiked Wheat Products[a]

product	% recovery[b] 0.1 ppm	0.5 ppm	1.0 ppm	5.0 ppm	10.0 ppm
whole wheat cereal	81, 87	91, 83	90, 90	92, 91	94, 93
whole wheat flour	88, 89, 78	89, 88	–	–	–
refined white flour	81, 85	87, 87	–	–	–

[a] Dashes indicate that no sample analyses were carried out. [b] Determined at 280 nm.

coextractive peak which was not present at the other wavelengths. Table I lists recoveries obtained for asulam spiked at various levels in the wheat products. Good results were obtained as low as 0.1 ppm, the lowest spiking level attempted. The minimum detectable level was estimated to be about 0.02 ppm in the products studied. The cereal samples were slightly cleaner than the flour samples when monitored at 268 nm. All chromatograms were similar at 280 nm.

The hexane partition in the sample clean up was necessary to remove lipophilic coextractives such as oils which would be strongly retained by the column. Also if this was not done, at 0.1 ppm the residue would not dissolve completely in the mobile phase resulting in a cloudy solution. This could not be cleared either by centrifugation or by filtration through Millipore filters. It is probable that passage of the solution through a small reversed-phase precolumn or a disposable Sep-Pak cartridge would remove this material while permitting the clear solution containing the asulam to pass through. For our purposes the hexane partitioning performed well and was thus incorporated into the cleanup procedure.

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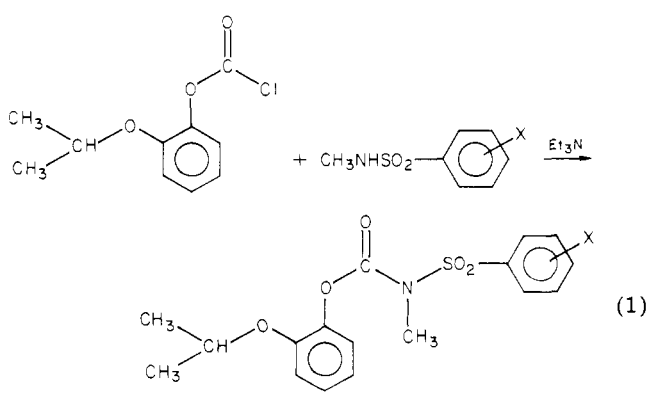
Insecticidal Properties of *N*-Sulfonyl Derivatives of Propoxur and Carbofuran

A series of substituted *N*-benzenesulfonyl derivatives of carbofuran and propoxur containing electron-withdrawing substituents on the benzene ring were synthesized and examined for toxicity to house flies and mosquito larvae. In general, the derivatives were noninsecticidal when tested alone, but some of the compounds were toxic to house flies when synergized with piperonyl butoxide. An explanation for the poor insecticidal activity and low mammalian toxicity of these derivatives is given.

Recent reports from this and other laboratories have described the favorable order of selectivity which is achieved when toxic methylcarbamate insecticides are derivatized by appropriate substitution of the hydrogen atom on the methylcarbamyl moiety. For example, replacement of the methylcarbamyl proton with acyl (Fraser et al., 1965), dialkoxyphosphinothioyl (Fahmy et al., 1970), alkyl- and arylsulfenyl (Black et al., 1973a), aminosulfenyl (Fukuto et al., 1975), and carbamylsulfenyl (Fahmy et al., 1974, 1978; Sousa et al., 1977) results in derivatives of generally low mammalian toxicity and high insecticidal activity. While a wide variety of sulfenyl derivatives of methylcarbamate insecticides have been examined for toxicological properties, little has been reported on the insecticidal activity of sulfur derivatives of higher oxidation state. In a previous report (Chiu et al., 1975), we described the poor insecticidal activity of a single arylsulfonyl derivative, the *N*-2-toluenesulfonyl derivative of carbofuran. The present study was conducted to determine whether derivatization with substituted benzenesulfonyl groups containing electron-withdrawing moieties would result in compounds with higher insecticidal activity.

EXPERIMENTAL SECTION

The *N*-arylsulfonyl derivatives of propoxur (2-isopropoxyphenyl methylcarbamate) and carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranyl methylcarbamate) were prepared by reacting the appropriate aryl chloroformate and ring-substituted methylbenzenesulfonamide according to eq 1 for a propoxur derivative. A typical procedure is



(1)

given as follows. To a chilled solution of 2.5 g of *p*-bromo-*N*-methylbenzenesulfonamide and 2.15 g of 2-isopropoxyphenyl chloroformate was added 1.75 g of triethylamine dropwise with stirring. After being stirred at room temperature for 2 h, the mixture was washed in turn with water, 5% hydrochloric acid, 5% aqueous sodium bicarbonate, and water, and the solution was dried over anhydrous sodium sulfate. Removal of the solvent gave

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